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Dependency of polyelectrolyte solvent composition on electrochromic photopic contrast

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ABSTRACT

Herein, we present a versatile way to increase the photopic contrast of electrochromic devices (ECDs), approximately 14%, through the use of binary mixtures of propylene carbonate, diethyl carbonate, and ethylene carbonate that serve the role as plasticizers in the gel electrolyte. The binary plasticizer mixture changed the physical properties of the gel electrolyte medium, including the viscosity and dielectric constant, and also facilitates the diffusion of ions and monomer in the medium leading to an increase in ionic conductivity and the photopic contrast. ECDs were fabricated using a one-step lamination procedure, based on poly(2,2-dimethyl-3,4-propylenedioxythiophene) (PProDOT-Me₂) with different polymer gel electrolyte compositions where the electrochromic polymer was electrochemically obtained *in situ*. Gel electrolytes based on unary or binary plasticizer systems and poly(ethylene glycol) diacrylate (PEG-DA) with varying lithium trifluoromethanesulfonate (LiTrif) loading were investigated for the effect of solvent on ionic conductivity and the resulting photopic contrast of the ECD. This study demonstrates a relationship between photopic contrast and ionic conductivity, where the system reaches a maximum in photopic contrast the system is also at the maximum ionic conductivity.

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1. Introduction

Conjugated polymers (CPs) have drawn interest in several different areas for industrial application such as organic transistors, sensors, light-emitting diodes, solar cells, batteries, and electrochromic devices [1–10]. CPs are suitable for electrochromic devices due to their low manufacturing cost, flexibility, chemical stability, fast switching time, optical memory, and high coloration efficiencies [11–16]. Furthermore, CPs can be tailored to generate different colors in their neutral state through modification of their structure, which results in a change in the energy band gap. The electrochromic color can change between a bleached (oxidized) state to a colored (neutral) state or between different colored states [13,17–19].

Polythiophene, polypyrrole, polyaniline, and their derivatives have been implemented in electrochromic devices due to open atmosphere processing techniques and high electrochromic contrast [20,21]. Poly(3,4-ethylenedioxythiophene) (PEDOT), a polythiophene derivative, has gained considerable attention for electrochromic devices due to PEDOT's low oxidation potential, high optical contrast,

and fast switching speed [22,23]. Another polythiophene derivative with even greater contrast, poly(2,2-dimethyl-3,4-propylenedioxythiophene) (PProDOT-Me₂), continues to be an exciting electrochromic material for such devices switching between purple in the neutral state and colorless transparent in the oxidized state [24]. Reynolds et al. reported that PProDOT-Me₂ has high contrast in the visible, NIR, and mid-IR regions [25], and that PProDOT-Me₂ lacked the typical large NIR absorption exhibited by conductive polymers resulting in a more transparent oxidized state that translates to improved contrast as well as a significant improvement of the switching speed attributed to faster ion movement. A one-step lamination procedure was reported by Invernale et al. described a simplistic approach to ECD fabrication [26,27]. More recently, ProDOT-Me₂ was copolymerized with 1,3-di-*t*-butylProDOT in a high throughput screening method to achieve copolymers spanning the entire single-wavelength subtractive spectrum [28]. In addition, long-term stability of a one-step lamination procedure using a ProDOT derivative was achieved [29], and the use of this method for large area ECDs was reported [30].

One way to achieve high photopic contrast of ECDs is through the tailoring of syntheses of new conjugated polymers [31–33]. An alternate pathway for improvement is variation of the polymer gel electrolyte composition. In general, a polymer gel electrolyte based

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solely on polymerization of oligoethylene glycol diacrylate in the presence of lithium salt results in low ionic conductivity (10^{-9} – 10^{-5} S cm $^{-1}$ at 25 °C) at room temperature due to ion diffusion attributed to the low viscosity of the medium [34]. Here, ionic conductivity and its role in photopic contrast is studied by varying the plasticizer within the polyelectrolyte gel matrix.

2. Experimental

2.1. Material

Lithium trifluoromethanesulfonate (LiTrif), dimethoxyphenylacetophenone (DMPAP), propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC), and poly (ethylene glycol) diacrylate (Mn=700) (PEG-DA), were purchased from Sigma-Aldrich and used as received. Indium doped Tin Oxide (ITO) coated glass 50 mm × 75 mm × 0.9 mm, $R_s=8$ – 15Ω was purchased from Delta Technologies and cleaned by sonication in acetone for 10 min followed by air drying.

2.2. Monomer synthesis

2,2-Dimethyl-3,4-propylenedioxythiophene (ProDOT-Me $_2$) was synthesized using a transesterification ring closure starting with commercially available 3,4-dimethoxythiophene and 2,2-dimethylpropane-1,3-diol (Sigma-Aldrich) according to the literature procedure [24].

2.3. Instrumental

A CL-1000 Ultraviolet Crosslinker was used to cure the gel electrolyte. All electrochemistry was performed using a CHI 400 or a CHI 660A potentiostats. Spectroelectrochemical studies were performed using a Cary 5000 UV–vis–NIR. The conductivity measurements were performed using a 4284A Precision LCR Meter.

2.4. Preparation of the gel electrolyte

All gel electrolytes were prepared by mixing a total of 5 g solvent, 5 g poly (ethylene glycol) diacrylate (Mn=700) (PEG-DA), 17.5 mg of photoinitiator (DMPAP) and LiTrif at different concentrations, 0.5 g to 1.5 g, and then sonicating for 15 min until dissolved. The study focused on three solvent systems at different LiTrif concentrations, 5 g PEG-DA, 17.5 mg DMPAP.

2.5. Construction of the electrochromic device

Electrochromic devices were fabricated using the *in situ* approach developed by our group [27]. The electroactive monomer (ProDOT-Me $_2$), 2.5 wt%, was mixed with the liquid electrolyte, and then this mixture was sandwiched between two ITO coated glass substrates. Sequentially, the electrolyte gel was cured using UV light at 320 μ W/cm 2 intensity for 5 min. To form the conjugated polymer, poly(2,2-dimethyl-3,4-propylenedioxythiophene) (PProDOT-Me $_2$), a potential of +3 V versus ground was applied to the device for 60 s to form the electrochromic polymer and then the device was cycled between ± 2 V versus ground to switch between the colored and bleached states.

2.6. Ionic conductivity measurement

The ionic conductivity, σ , of the solid polymer gel electrolytes was evaluated by AC impedance spectroscopy over a frequency range of 20 Hz to 100 kHz. The solid-gel electrolytes were prepared as described previously (Section 2.4), sandwiched between

two stainless steel electrodes, and the impedance as a function of frequency was determined. The solid electrolyte resistance (R) was obtained from the plots of $\log Z$ against $\log f$ (Bode plots) where Z and f are the impedance and frequency, respectively. The ionic conductivity of the solid gel electrolyte was then calculated using the equation $\sigma=t/RA$, where t is the thickness of the solid electrolyte and A is the electrolyte contact area with the electrodes. The solid gel electrolytes for all systems in this study have the same thickness 0.7 mm.

3. Results and discussion

Propylene carbonate is the most commonly used plasticizer for preparing electrolyte gels for ECDs due to its high dielectric constant (64.92 at 25 °C), high boiling point (241 °C), low freezing point (–49 °C), and ability to dissolve lithium salts. The effect of different plasticizers as well as binary mixtures with propylene carbonate on the ionic conductivity of the solid-gel electrolyte was investigated and the resulting photopic contrast of the ECD was then measured. The photopic contrasts reported here are for the entire visible spectrum and not for a single wavelength, allowing for a measurement more representative of the human eye's response. The photopic contrast $T_{photopic}$ is calculated from the equation:

$$T_{photopic} = \frac{\int_{\lambda_{min}}^{\lambda_{max}} T(\lambda)S(\lambda)P(\lambda)d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} S(\lambda)P(\lambda)d\lambda}$$

where $T(\lambda)$ is the spectral transmittance of the device, $S(\lambda)$ is the normalized spectral emittance of the light source, and $P(\lambda)$ is the normalized spectral of the eyes. λ_{min} and λ_{max} define the considered range of wavelengths between 380 nm and 720 nm. All $T_{photopic}$ measurements reported here are without background correction.

For system 1, the control system, the photopic contrast increases as the concentration of salt increases reaching a maximum value of 43% at 9.09 wt% LiTrif as shown in Fig. 1 (see Table 1 in Supporting information). At salt concentrations exceeding 9% there was a decrease in ionic conductivity attributed to salt aggregation (Fig. 1) [35]. The photopic contrast saturates with a small change in the ionic conductivity when going from a salt concentration of 7.41 wt% to 9.91 wt% Tables 1 and 2.

As shown in Fig. 2, the solid-state gel electrolyte prepared in system 2(A) is opaque in comparison to the transparent system 1 making it unsuitable for electrochromic devices. The variation of ionic conductivity with respect to the concentration of LiTrif was

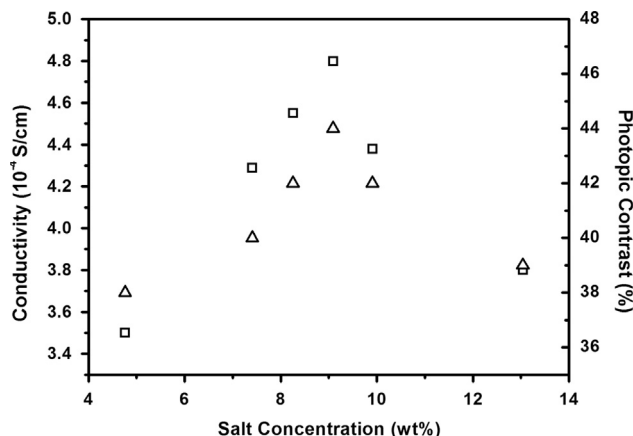


Fig. 1. Ionic conductivities (open square) and ECDs photopic contrasts (open triangle) for system 1 (consisting of PC).

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